Chiral (SO)–N–(SO) Sulfoxide Pincer Complexes of Mg, Rh, and Ir: N–H Activation and Selective Sulfoxide Reduction upon Ligand Coordination

Locke, Harald ; Herrera, Alberto ; Heinemann, Frank W ; Linden, Anthony ; Frieß, Sibylle ; Schmid, Bernhard ; Dorta, Romano

Abstract: Multigram quantities of the optically pure amino−bis-sulfoxide ligand (S,S)-bis(4-tert-butyl-2-(ptolylsulfinyl) phenyl)amine ((S,S)-3) are accessible by in situ lithiation of bis(2-bromo-4-tert-butylphenyl)amine (1) followed by a nucleophilic displacement reaction with Andersen's sulfinate 2. Deprotonation of (S,S)-3 with MgPh2 yields the magnesium amido−bis-sulfoxide salt (S,S)-4 quantitatively. Metathetical exchange of (S,S)-4 with [RhCl(COE)2]2 affords the optically pure pseudo-C2-symmetric Rh(I)−amido bissulfoxide pincer complex mer-(R,R)-[Rh(bis(4-(tert-butyl)-2- (p-tolylsulfinyl)phenyl)amide)(COE)] (mer-(R,R)-5). This complex reacts with 3 equiv of HCl to give the facial Rh(III) complex fac-(S,R,R)-[Rh(bis(4-(tert-butyl)-2-(p-tolylsulfinyl)- phenyl)amine)Cl3] (fac-(S,R,R)-6), in which one of the sulfoxide functions has been reduced to the sulfide and in which the resulting sulfoxide−sulfide−amine ligand is facially coordinated. The same complexes 5 and 6 form in a 1:2 ratio in a disproportionation reaction when [RhCl(COE)2]2 is treated with 2 equiv of neutral ligand 3. N−H activation is directly observed in the reaction of [IrCl(COE)2]2 with 3, affording the amido−hydrido−Ir(III) complex [Ir(bis(4-(tert-butyl)-2-(ptolylsulfinyl) phenyl)amide)(Cl)(H)(COE)] (8).

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Chiral (SO)–N–(SO) sulfoxide pincer complexes of Mg, Rh, and Ir: N–H activation and selective sulfoxide reduction upon ligand coordination

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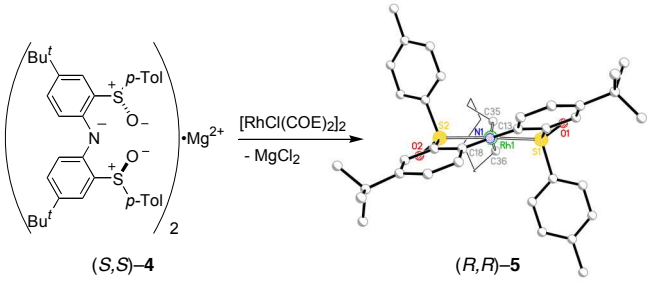
Abstract



Multi–gram quantities of the optically pure amino–bissulfoxide ligand (*S*,*S*)–bis(4–*tert*–butyl–2–(*p*–tolylsulfinyl)phenyl)amine ((*S*,*S*)–**3**) are accessible by *in situ* lithiation of bis-(2-bromo-4-*tert*-butylphenyl)amine **1** followed by a nucleophilic displacement reaction with Andersen's sulfinate **2**. Deprotonation of (*S*,*S*)–**3** with $MgPh_2$ yields the magnesium amido–bissulfoxide salt (*S*,*S*)–**4** quantitatively. Metathetical exchange of (*S*,*S*)–**4** with $[RhCl(COE)_2]_2$ affords the optically pure pseudo C_2–symmetric Rh(I)–amido bisulfoxide pincer complex *mer*–(*R*,*R*)–[Rh(bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amide)(COE)] (*mer*–(*R*,*R*)–**5**). This complex reacts with 3 equiv of HCl to give the facial Rh(III) complex *fac*–(*S*,*R*,*R*)–[Rh(bis(4-(*tert*-butyl)-2-(*p*-tolylsulfinyl)phenyl)amine)Cl_3] (*fac*–(*S*,*R*,*R*)–**6**), in which one of the sulfoxide functions has been reduced to the sulfide, and where the resulting sulfoxide–sulfide–amine ligand is facially coordinated. The same complexes **5** and **6** form in a 1:2 ratio in a disproportionation reaction when $[RhCl(COE)_2]_2$ is treated with 2 equiv of neutral

ligand **3**. N–H activation is directly observed in the reaction of $[IrCl(COE)_2]_2$ with **3**, affording the amido–hydrido–Ir(III) complex [Ir(bis(4-(*tert*-butyl)-2-(*p*-tolylsulfinyl)phenyl)amide)(Cl)(H)(COE)] **8**.

Introduction

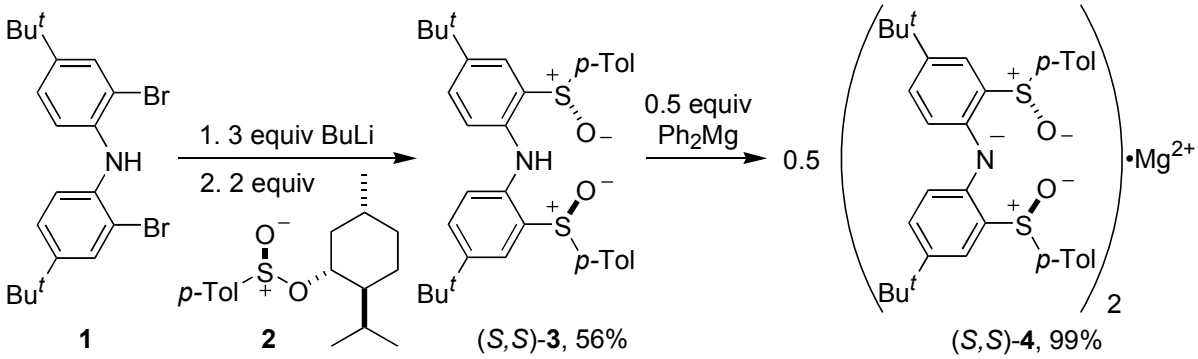
Pincer ligands give rise to stable complexes thanks to a tridentate coordination mode and the usually anionic nature of the central donor atom. The meridional, T-shaped configuration forms a rigid scaffold perfectly suited for the introduction of chirality in pincer donor moieties, such as oxazolines or stereogenic phosphines in order to create coordination environments with local C_2-symmetry.[1] The introduction of chiral sulfoxides as the pincer donor function has rarely been attempted in this context, even though chiral sulfoxides emerged as competent ligands for asymmetric catalysis.[2] Evans and coworkers synthesized racemic bis-sulfoxide (SO)–C–(SO) pincer complexes of Pd(II) exhibiting C_2-symmetric coordination geometries.[3] We reasoned that the rigid diarylamido scaffold, so widely and successfully used in PNP pincer complexes,[4] should also be readily amenable to functionalization by optically pure sulfinates to afford the corresponding chiral bis-sulfoxide pincer ligands. Here, we wish to communicate the synthesis of the first example – as far as we know – of an optically pure chiral sulfoxide-based (SO)–N–(SO) pincer ligand and some exploratory coordination chemistry with Mg, Rh, and Ir.

Results and discussion

Scheme 1 outlines the synthesis of the ligand and its magnesium salt. Bis-(2-bromo-4-*tert*-butylphenyl)amine **1** was obtained by bromination of bis-(4-*tert*-butylphenyl)amine in excellent yield[5] and then lithiated at low temperature with three equivalents of BuLi in Et_2O solution. The tris-lithiated product was used *in situ* in a nucleophilic displacement reaction with Andersen's sulfinate **2**[6] at 210 K. The optically and analytically pure amino-bis-sulfoxide **3** was isolated in moderate yields[7] after column chromatography and recrystallization. Finally, deprotonation of **3** with diphenylmagnesium in benzene solution afforded the magnesium salt **4** quantitatively and in analytically pure form.[8] **4** turned out to be highly soluble in benzene, and its ^{1}H–NMR spectrum confirmed the deprotonation of the amine function. The resonances of the *ortho*–protons of the *p*–tolyl groups appear downfield at 8.01 ppm when compared to 7.49 ppm in neutral **3**, which hints at a Mg(II)–sulfoxide coordination, whereas the proton signals from the aromatic backbone are shifted on average up-field, in accordance with the presence of an electron rich amide function. While **4** only forms amorphous powders, single crystals of **3** were grown for an X-ray diffraction analysis. The two molecules of the asymmetric unit show only

minor structural differences, and the absolute configurations of the sulfur atoms are (*S*,*S*), as expected (see Figure 1). An intramolecular N–H···O hydrogen bond is present between oxygen atom O2 and the proton attached to N1 with an H···O contact of 2.07(3) Å. This proton is characterized by a resonance at 8.61 ppm in the NMR spectrum in C_6D_6 solution. The dihedral angle between the planes of the two aromatic rings C8-C13 and C18-C23 measures 47.4(2)° (43.0(2)° in the second molecule), and is probably the result of steric repulsion between the hydrogen atoms attached to carbons C12 and C19, which are 2.20 Å apart (2.18 Å for the second molecule). The sulfur-oxygen and the sulfur-carbon bond distances range between 1.496(2)–1.506(2) Å and 1.788(2)–1.800(2) Å, respectively, across both independent molecules.

Scheme 1. Syntheses of the neutral ligand **3** and its Mg-salt **4**



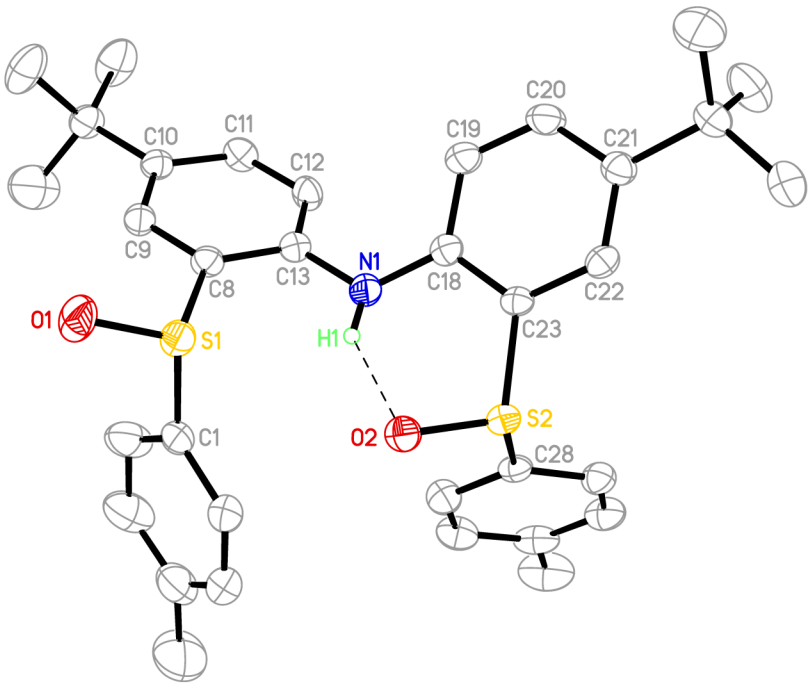
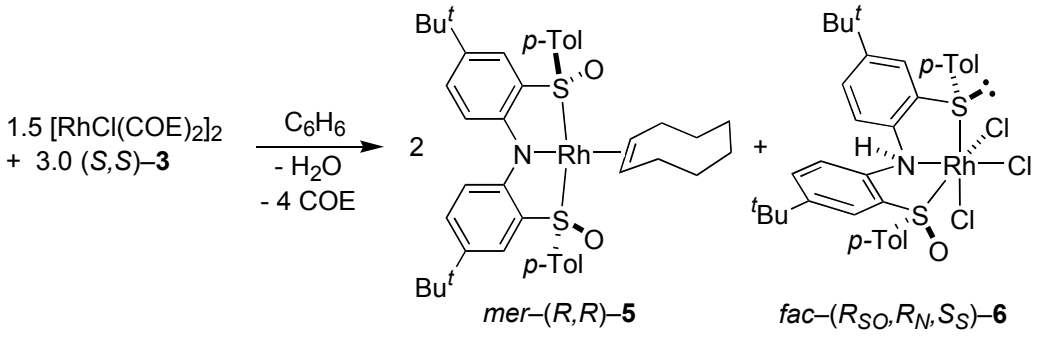
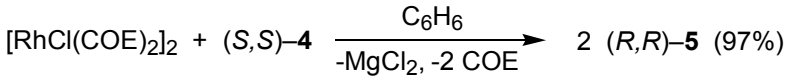


Figure 1. The molecular structure of one of the two symmetry-independent molecules of (*S,S*)–**3** in the crystal drawn with 50% probability displacement ellipsoids. For clarity, most H-atoms have been omitted and only one conformation of the disordered *t*-Bu group at C4 is shown. Selected bond lengths (Å) and angles (°) are: S1–O1, 1.496(2); S1–C2, 1.800(2); S1–C13, 1.798(3); S2–O2, 1.506(2); S2–C8, 1.789(2); S2–C28, 1.794(2); N1–C13, 1.396(3); N1–C18, 1.395(3); O1–S1–C8, 106.4(1); O1–S1–C1, 106.5(1); C1–S1–C8, 97.4(1); O2–S2–C23, 107.49(9); O2–S2–C28, 106.36(9); C23–S2–C28, 100.7(1); C13–N1–C18 125.1(2).

The coordination chemistry of the neutral ligand **3** was explored by reacting it with $[RhCl(COE)_2]_2$ (COE = cyclooctene) in benzene solution. This resulted in a clean disproportionation reaction that formed two Rhodium complexes, as outlined in eq 1. The formation of 2.0 equiv of the highly soluble Rh(I) complex **5** was determined with good precision by ^{1}H-NMR in the presence of 1,4-dioxane as the internal standard. Most of complex **6** swiftly precipitated out of solution as orange crystals within *ca*. 3 h. In **6** the metal suffered a two-electron oxidation while one sulfoxide group was reduced to the corresponding thioether. Complex **5** was also prepared independently by metathetical exchange of $[RhCl(COE)_2]_2$ with the Mg–salt **4** according to eq 2 and isolated as an analytically pure, air-sensitive orange powder in almost quantitative yield. NMR spectroscopy confirmed its identity with complex **5** of eq 1. The spectra display no diastereotopic resonances for the sulfoxide pincers, which is in agreement with local C_2–symmetry. In contrast, the resonances of the vinylic protons of the coordinated COE are split into two mulitplets centered at 4.32 ppm and 3.95 ppm. The aromatic signals are, on average, shifted slightly downfield when compared to those of the magnesium salt **4**.



(1)



(2)

The X-ray crystal structure of one of two very similar, symmetry–independent molecules of **5** is depicted in Figure 2. The coordination geometry around rhodium is pseudo square planar. The meridional tridentate ligand is held in place by the central amide function and the two stereogenic sulfur pincers impose an effective local C_2-symmetry. The S-bound sulfoxide moieties[9] show the expected (*R*) configurations. Together with the perfectly planar amide tether (sum of angles around N: 360°) they coordinate Rh to give fused five membered chelate rings, which are twisted significantly out of co-planarity along with the aromatic rings C8–C13 and C18–C23 with a dihedral angle of 37.99(7)° (36.99(9)° for the other molecule).[10] Cyclooctene coordination to Rh is perpendicular with respect to the coordination plane, and the double bond is slightly elongated to 1.381(5) Å due to π-back–bonding from the metal center.

The reaction of eq 1 was also run on a preparative scale in benzene in order to recover analytically pure orange crystals of **6** in 95% yield by simple filtration (complex **5** is highly soluble in benzene). Surprisingly, crystals of **6** are quite air sensitive. An X-ray diffraction analysis revealed the presence of two structurally very similar homochiral molecules of **6** in the asymmetric unit, and Figure 3 shows the ORTEP of one of them. The pseudo-octahedral Rh(III) center is facially coordinated by the tridentate (SO)-N-S ligand. The protonation of the perfectly planar sp^2–amide in **5** (*vide supra*) to an sp^3–amine endows the ligand with the necessary flexibility for the *mer* to *fac* rearrangement that is observed in **6**.[11] Indeed, the N1 atom has an (*R*)–configuration and is trigonal pyramidal with the angles between the bonds to C13, C18, and Rh1 summing 335°. The Rh-amine distance is the shortest coordination bond at 2.078(4) Å and is slightly longer than the Rh-amide bond in **5** (2.050(2) Å). While the rhodium-chloride bond lengths are essentially equivalent, the Rh–S distances of the sulfoxide and sulfide functions differ significantly at 2.230(1) Å and 2.299(1) Å, respectively. The S-O bond distance of 1.461(2) Å is *ca*. 0.04 Å shorter than in the free ligand **3**, as is commonly observed in sulfur–bound metal sulfoxide complexes.[12] The partial reduction of the ligand within the coordination sphere of Rh is a stereoselective process, and the structure shows an unchanged absolute (R_{SO})–configuration of the sulfoxide and an (S_S)–configuration of the sulfide function, which is roughly trigonal pyramidal with the bond angles around S2 summing to 315°. The diastereomeric purity found in the crystal may be due to steric or packing forces because coordinated unsymmetrical sulfides are stereochemically non-rigid.[13] In fact, NMR spectra of dissolved crystals of (R_{SO},R_N,S_S)–**6** reveal the presence of a minor isomer (CD_2Cl_2: 15%, THF-D_8: 10%),[14] which we believe to be the (R_{SO},R_N,R_S)–diastereomer. The two isomers are characterized by their broad N–H resonances at 9.27 ppm (major) and 9.06 ppm (minor).

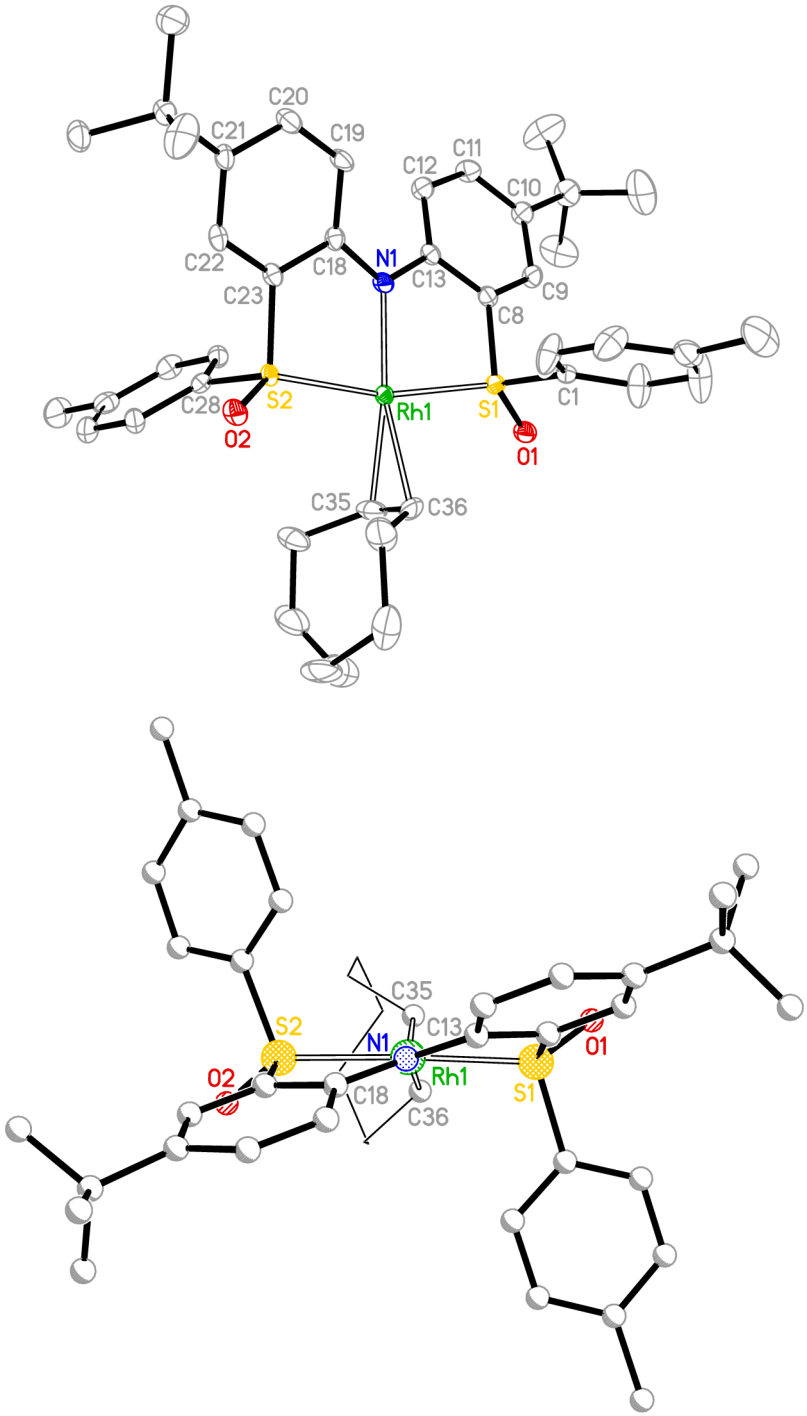


Figure 2. The molecular structure of one of two symmetry-independent molecules of (*R*,*R*)–**5** drawn with 50% probability displacement ellipsoids and a ball & stick view along the N1–Rh1 vector exhibiting the approximate local C_2-symmetry and the out-of-plane twist of the diarylamido backbone. Selected bond lengths (Å) and angles (°) are: Rh1—N1 2.050(2); Rh1—C35 2.164(3); Rh1—C36 2.184(3); Rh1—S1 2.2366(7); Rh1—S2 2.2526(7); S1—O1 1.472(2); S1—C8 1.781(3); S1—C1 1.796(3); S2—O2 1.479(2); S2—C23 1.775(3); S2—C28 1.793(3); N1—C13 1.388(3); N1—C18 1.388(3); C35—C36 1.381(5); N1—Rh1—C35 160.2(2); N1—Rh1—C36 162.0(1); N1—Rh1—S1 83.07(7); C35—Rh1—S1 95.42(9); C36—Rh1—S1 91.01(9); N1—Rh1—S2 82.93(7); C35—Rh1—S2 98.51(9); C36—Rh1—S2 101.71(9); S1—Rh1—S2 165.82(3); O1—S1—Rh1 126.62(8); C1—

S1—Rh1 108.5(1); C8—S1—Rh1 100.52(9); O2—S2—Rh1 126.40(9); C23—S2—Rh1 100.57(9); C28—S2—Rh1 110.58(9); C13—N1—C18 123.1(2); C13—N1—Rh1 118.1(2); C18—N1—Rh1 118.8(2).

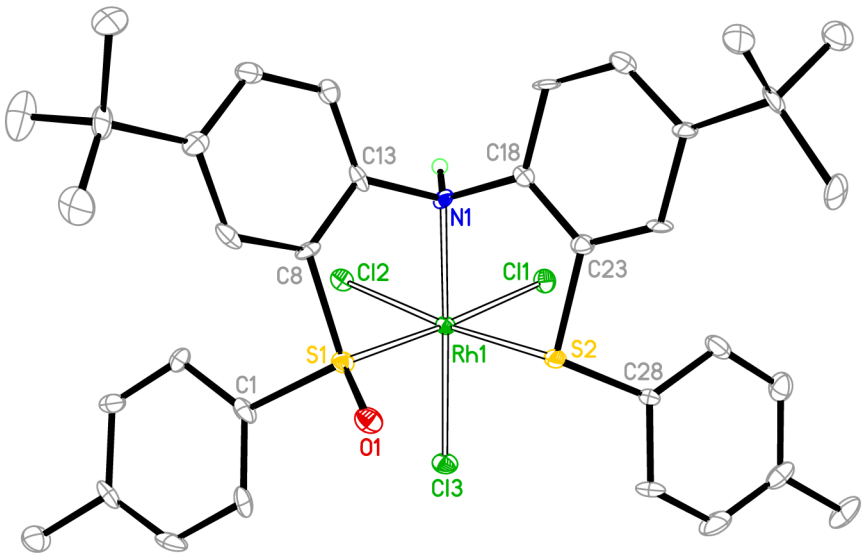
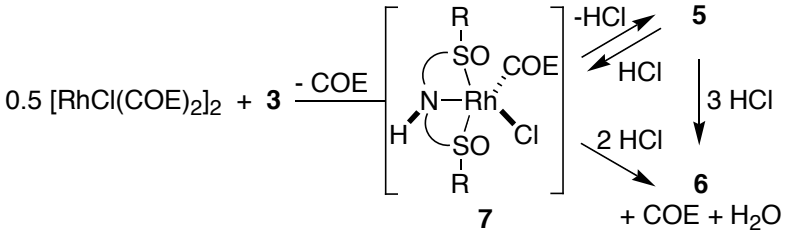


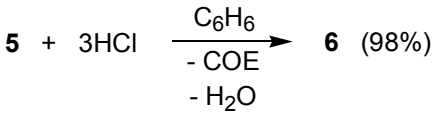
Figure 3. The molecular structure of one of two independent molecules of (R_{SO},R_N,S_S)-**6** in the crystal, drawn with 50% probability displacement ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Rh1–S1, 2.230(1); Rh1–S2, 2.299(1); Rh1–N1, 2.078(4); Rh1–Cl1, 2.330(1); Rh1–Cl2, 2.350(1); Rh1–Cl3, 2.333(1); S1–O1, 1.461(2); S1–C1, 1.792(5); S1–C8, 1.791(4); S2–C23, 1.786(5); S2–C28, 1.753(5); N1–H1, 0.8406; N1–C13, 1.495(6); N1–C18, 1.475(6); Cl1–Rh1–Cl2, 89.06(4); S1—Rh1—S2 88.25(4); O1–S1–Rh1, 118.35(9); C8—S1—Rh1 99.3(2); C1—S1—Rh1 116.3(2); C8—S1—C1 104.4(2); C23—S2—Rh1 97.7(2); C28—S2—Rh1 112.2(2); C23—S2—C28 105.1(2); C13—N1—Rh1 112.3(3); C18—N1—Rh1 112.5(3); C13–N1–C18, 110.5(3).

A plausible reaction sequence of the disproportionation reaction of eq 1 is outlined in Scheme 2. $[RhCl(COE)_2]_2$ and the amino-disulfoxide ligand **3** first form a Rh(I)–amino adduct such as **7**, which stands in a HCl elimination-addition equilibrium with the Rh(I)–amide **5**. This equilibrium concentration of HCl successively reacts with **7** to afford **6**, which precipitates out of solution and **thus** drives the equilibrium to products **5** and **6** in a 2:1 ratio. Such a mechanism implies the presence of free HCl in the reaction mixture, and indeed, when 3 equiv of HCl (as its solution in dry methylcyclopentylether) were reacted with **5** (prepared according to eq 2) in benzene, complex **6** almost quantitatively precipitated as orange crystals (eq 3). The mother liquor of this reaction contained trace amounts of unreacted **5** and **6**, along with 1 equiv of COE. Water was qualitatively detected by Karl-Fischer titration. Neither in the disproportionation reaction with the neutral ligand (eq 1), nor in the reaction of **5** with HCl (eq 3) were we able to directly detect a Rh(III)–hydride species[15]

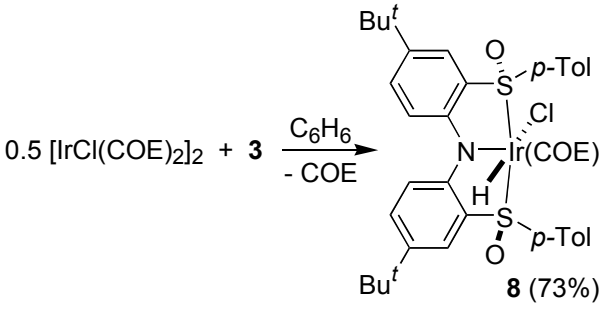
that would form from **7** *via* N–H activation. However, when N–deuterated ligand **3**–*d* was used for the reaction of eq 1 partial deuteration of all C–H bonds of COE was observed in the D-NMR spectrum, indicative of a transient "ring walking" Rh(III)–D/H species. Isolation of a corresponding amido-hydrido species was possible by switching to iridium, and smooth N–H activation according to eq 4 yielded complex **8**, characterized by a singlet hydride resonance at -15.2 ppm in the NMR spectrum.[16] The vinylic COE–protons and the two halves of the pincer ligand are diastereotopic exhibiting differing sets of resonances. It is reasonable to assume a meridional geometry and π–coordination of COE *trans* to the electron-rich amide function. We suggest S-coordination of the sulfoxide functions due to the formation of favorable five-membered chelate rings.

Scheme 2. Proposed reaction sequence producing **5** and **6** in a 2 : 1 ratio (*cf.* eq 1)





(3)



(4)

In conclusion, the optically pure sulfoxide-based pincer ligand **3** is readily accessible on a multi–gram scale, and the crystal structure of the Rh(I)–complex **5** evidences its very effective C_2–symmetric

coordination mode. When $[RhCl(COE)_2]_2$ is complexed with the neutral ligand **3**, the presence of its N–H function causes a disproportionation reaction in which one of the coordinated sulfoxides is selectively reduced to the corresponding sulfide with concomitant oxidation of the metal center. The same reduction of the ligand was also achieved by treating the Rh(I) pincer complex **5** with HCl. In both reactions, the protonation of the ligand amide function triggers a *mer–fac* coordination switch. The directly observed partial reduction of ligand **3** in complex **6** might bear some relevance to the fact that chiral sulfoxide ligands work well in certain metal–catalyzed asymmetric C–C bond forming reactions,[17] but are prone to reduction (and thus loss of chirality) under more strongly reducing conditions, such as hydrogenations.[18] Metal complexes, such as the ones disclosed here, bearing ligand **3** and variations thereof are currently being tested in catalytic reactions, and results will be reported in due course.

Experimental Section

All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glove box techniques, unless otherwise stated. THF, Et_2O, and benzene were distilled from purple Na/Ph_2CO solutions, toluene from Na, pentane, C_6D_6, and THF-D_8 from Na_2K alloy, CH_3CN, CH_2Cl_2, and CD_2Cl_2 from CaH_2, NEt_3 and 1,4-dioxane from K. $CDCl_3$ was degassed with three freeze-pump-thaw cycles and then kept over activated molecular sieves (4 Å) in a glove box. Commercial 2.5 M BuLi in hexanes was dissolved in hexane to 1.18 M, filtered (Whatman GF/B glass fiber), and titrated with the Suffert method before use.[19] 3.0 M HCl in cyclopentylmethylether was purchased from Aldrich Corp. and the bottle openend and used in a glovebox. *p*–Tolyl-menthylsulfinate (**2**),[6] bis(2-bromo-4-(*t*-butyl)phenylamine (**1**),[5] $[RhCl(COE)_2]_2$, $[IrCl(COE)_2]_2$,[20] and diphenylmagnesium[21] were prepared according to published procedures. Elemental analysis samples of air sensitive compounds were handled in a glove box. NMR spectra were recorded on a Jeol Lambda/Eclipse 400MHz spectrometer, and the solvent residual signals were used as internal reference for the ^{1}H-NMR-spectra.[22]

(*S*,*S*)–Bis(4–(*tert*–butyl)–2–(*p*–tolylsulfinyl)phenyl)amine ((*S*,*S*)–3). *n*-Butyl lithium (50.0 ml, 1.18 M in hexane) was added dropwise to a cooled solution (210 K) of bis(2-bromo-4-(*tert*-butyl)phenyl)amine **1** (8.64 g, 19.7 mmol) in diethyl ether (150 ml). The resulting yellow solution was allowed to warm to RT and was then stirred for 4 h. The solution was again cooled to 210 K, at which temperature (*S*)-menthyl *p*-toluene-sulfinate **2** (11.6 g, 39.3 mmol) dissolved in in ether (170 ml) was slowly added under stirring. The resulting orange reaction mixture was allowed to warm to RT and

stirring was continued for 24 h. After evaporating the reaction mixture to dryness, ether (160 ml) and water (160 ml) were added, and the pH adjusted to below 7 with ammonium chloride. The organic layer was separated, washed with brine (2 × 40 ml), dried over Na_2SO_4, and filtered. The volatiles were evaporated *in vacuo* for 13 h to afford a yellow–brown oil. Column chromatography (Merck silica gel G60, hexane/EtOAc = 10:1, V/V), followed by washing with hexane and recrystallization from THF/pentane yielded white crystalline material (6.42 g, 57%). X–ray quality single crystals were grown by vapor diffusion of pentane into a THF-solution of **3**. Elemental analysis found: C, 73.52; H, 7.13; N, 2.52; S, 11.31. Calcd. for $C_{34}H_{39}NO_2S_2$: C, 73.21; H, 7.05; N, 2.51; S, 11.49. $[\alpha]_D$ = -94.1° (*c* 1.05, THF, 294 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.74 (3H, m), 7.21–7.10 (10H, m), 6.46 (2H, d), 2.29 (6H, s), 1.32 (18H, s); (270 MHz, C_6D_6): δ 8.61 (1H, s), 7.89 (2H, d, *J* = 2.4 Hz), 7.49 (4H, d, *J* = 8.2 Hz), 6.84 (2H, dd, *J* = 2.4 Hz, *J* = 6.2 Hz), 6.71 (4H, d, *J* = 8.1 Hz), 6.46 (2H, d, *J* = 8.5 Hz), 1.78 (6H, s), 1.09 (18H, s). ^{13}C-NMR (67.8 MHz, C_6D_6) δ 147.68, 145.05, 143.25, 143.00, 137.02, 132.26, 131.53, 128.08, 126.32, 123.37, 36.95, 33.80, 23.50.

Magnesium–(*S*,*S*)–bis(4–(*tert*–butyl)–2–(*p*–tolylsulfinyl)phenyl)amide ((*S*,*S*)–4). Bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amine **3** (1.00 g, 1.74 mmol) and diphenyl magnesium ($Ph_2Mg{\cdot}0.8Et_2O$, 207 mg, 0.870 mmol) were placed in a vial and benzene (10 ml) was added. The mixture was stirred for 3 h and a yellow solution was obtained. The solvent was removed *in vacuo* to yield quantitatively a yellow powder (1.02 g, 99%). Elemental analysis found: C, 72.64; H, 6.75; N, 2.62; S, 11.03. Calcd. for $C_{68}H_{76}MgN_2O_4S_4(C_6H_6)_{0.5}$: C, 72.46; H, 6.77; N, 2.38; S, 10.90. ^{1}H NMR (400 MHz, C_6D_6): δ 8.01 (4H, d, *J* = 8 Hz), 7.56-7.55 (2H, m), 6.92-6.86 (2H, m), 6.72 (4H, d, *J* = 8 Hz), 1.78 (6H, s), 1.13 (18H, s). The spectrum indicates the presence of *ca*. 0.5 equiv of C_6H_6 of co-crystallization. ^{13}C-NMR (67.8 MHz, C_6D_6) δ 156.7, 141.3, 137.7, 135.2, 128.1. 128.0, 127.8, 127.6, 123.9, 122.9, 122.3, 31.9, 29.6, 19.04.

NMR-scale experiment producing 5 & 6 (eq 1) with 1,4-dioxane as the internal standard: Bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amine **3** (63.1 mg, 0.109 mmol) and $[RhCl(COE)_2]_2$ (39.1 mg, 0.0545 mmol) were mixed in a vial, and 0.3 mL of C_6D_6 were added. The resulting deep red solution was left undisturbed overnight to afford large amounts of crystals of **6**. The mixture was frozen (-34 °C), 1,4-dioxane (33.6 mg, 0.381 mmol) added, and after thawing at room temperature the red supernatant solution was decanted off the crystals into an NMR tube. The crystals were washed with 2 portions of C_6D_6 (0.2 mL), and the washings were added to the NMR tube. The ^{1}H NMR spectrum shows signals corresponding to 2.0 equiv of complex **5**, traces of complex **6** (low solubility in benzene), and dioxane in a 1:5.20 ratio.

***mer*–(*R,R*)–[Rh(bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amide)(COE)] (*mer*–(*R,R*)–5).** A solution of magnesium (*S,S*)–bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amide (*S,S*)–**4** (150 mg, 0.132 mmol) in benzene (2.5 mL) was added dropwise to a stirred suspension of $[RhCl(COE)_2]_2$ (94.7 mg, 0.132 mmol) in benzene (2.5 mL). The resultant deep red solution was stirred overnight, after which a fine precipitate was observed, which was filtered off (Whatman GF/B) and extracted with benzene (3 x 2 mL). The combined filtrates were evaporated to dryness, washed with pentane (2 × 5 ml), and dried *in vacuo* to give 197 mg (97 %) of an orange powder. Crystals suitable for an X-ray crystal-structure analysis were grown by vapor diffusion of pentane into a saturated benzene solution of **5**. Elemental analysis found: C, 67.09; H, 7.15; N, 1.81; S, 7.80. Calcd. for $C_{42}H_{52}NO_2RhS_2 \cdot (C_5H_{12})_{0.8}$: C, 66.76; H, 7.50; N, 1.69; S, 7.75. ^{1}H NMR (400 MHz, C_6D_6): δ 8.49 (4H, d, *J* = 8.3 Hz), 7.89 (2H, d, *J* = 2.3 Hz), 7.63 (2H, d, *J* = 8.8 Hz), 7.11 (2H, dd, *J* = 8.8 Hz, *J* = 2.2 Hz), 6.71 (4H, d, *J* = 8.4 Hz), 4.79- 4.72 (1H, m), 4.42-4.36 (1H, m), 2.94-2.89 (1H, m), 2.43-2.39 (1H, m), 2.19-2.11 (1H, m), 2.10-1.97 (1H, m), 1.78 (6H, s), 1.62-1.58 (1H, m), 1.45-1.41 (1H, m), 1.35-1.11 (6H, m), 1.09 (18H, s). The spectrum indicates the presence of 0.6 equiv of pentane. ^{13}C NMR (67.8 MHz, C_6D_6) δ 150.2, 144.9, 142.1, 141.7, 141.4, 130.9, 130.2, 127.6, 124.7, 121.7, 114.5, 80.3 (m), 34.4, 34.18, 31.4, 31.3, 31.1, 30.1, 29.7, 26.8, 26.3, 22.7, 21.0.

***fac*–(*S,R,R*)–[Rh(bis(4-(*tert*-butyl)-2-(*p*-tolylsulfinyl)phenyl)amine)Cl_3] (*fac*–(*S,R,R*)–6), Method A:** A solution of (*S,S*)–bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amine **3** (300.7 mg, 0.522 mmol) in benzene (1.5 mL) was added to a suspension of $[RhCl(COE)_2]_2$ (187.1 mg, 0.261 mmol) in benzene (1.5 mL). The final deep red solution was left undisturbed overnight, after which crystals had formed that were also suitable for an X-ray diffraction analysis. The red mother liquor was decanted off and the crystals were washed with benzene (2 x 1.5 mL) and pentane (2 x 1.5 mL). Drying *in vacuo* afforded 124 mg (95%) of slightly turbid yellow crystals. Elemental analysis found: C, 55.64; H, 5.37; N, 1.82; S, 8.06. Calcd. for $C_{34}H_{39}Cl_3NORhS_2 \cdot (C_6H_6)_{0.33}$: C, 55.64; H, 5.32; N, 1.80; S, 8.25. ^{1}H NMR (400 MHz, CD_2Cl_2), major diastereomer: δ 9.39 (1H, s, broad), 8.28 (1H, d, *J* = 8.7 Hz), 7.93 (1H, d, *J* = 8.9 Hz), 7.88 (2H, d, *J* = 8.5 Hz), 7.69 (1H, dd, *J* = 2.1 Hz, *J* = 8.6 Hz), 7.47 (1H, dd, *J* = 2.1 Hz, *J* = 8.8 Hz), 7.30 – 7.40 (6H, m), 7.12 (1H, d, *J* = 8.1 Hz), 2.47 (3H, s), 2.33 (3H, s), 1.20 (9H, s), 1.18 (9H, s); minor diasteromer: δ 9.15 (1H, s, broad), 8.1-8.2 (2H, m), 7.70-7.74 (1H, m), 7.55 (1H, m), 7.22-7.30 (2H, m), 6.94-7.05 (4H, m), 2.37 (3H, s), 2.27 (3H, s), 1.25 (9H, s), 1.17 (9H, s), other signals overlap with the major diastereomer. The spectrum shows *ca*. 0.33 equiv of co-crystallized benzene. ^{13}C NMR (67.8 MHz, THF-d_8) δ 153.7, 148.8, 148.5, 144.5, 143.6, 141.4, 135.2, 133.4 (2C),

133.0, 132.3, 131.6 (2C), 130.6, 129.4 (2C), 129.3, 129.0, 128.8 (2C), 128.2, 127.1, 126.6, 125.7, 35.7, 31.2 (3C), 31.1 (3C), 21.5, 21.4.

***fac*–(*S,R,R*)–[Rh(bis(4-(*tert*-butyl)-2-(*p*-tolylsulfinyl)phenyl)amine)Cl_3] (*fac*–(*S,R,R*)–6), Method B:** To a solution of complex (*R,R*)–**5** (100 mg, 0.122 mmol) in benzene (1.5 mL) were added 121 μL of a 3.0 M solution of HCl in cyclopentylmethylether. After 15 min yellow crystals began to form, and the mixture was left undisturbed for 24 h. The red-brown mother liquor was decanted off, and the crystals were washed with benzene (2 x 0.5 mL) and pentane (3 x 1 mL). HV drying for 30 min afforded 93 mg of opaque orange crystals (98%). NMR spectra of this compound in CD_2Cl_2 and THF-d_8 correspond to those obtained by method A and show 2.3 equiv of co-crystallized benzene.

[Ir(bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amide)(Cl)(H)(COE)] (8). A solution of bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amine (**3**, 350 mg, 0.608 mmol) in benzene (10 ml) was added dropwise to a stirred suspension of $[IrCl(COE)_2]_2$ (272 mg, 0.304 mmol) in benzene (5 ml). The resulting orange solution was stirred for 3 h and then evaporated to dryness. The solid was washed with pentane (3 × 10 ml) and dried in *vacuo* to yield an orange powder (395 mg, 73%). Elemental anal. calcd for $C_{42}H_{53}ClIrNO_2S_2(CH_3C_6H_5)_{0.8}$: C, 58.76; H, 6.09; N, 1.46; S, 6.67. Found: C, 58.94; H, 6.28; N, 1.53; S, 6.85. ^{1}H NMR (400 MHz, C_6D_6): δ 8.05-7.91 (6H, m), 7.68 (1H, d, *J* = 2.4 Hz), 7.63 (1H, d, *J* = 2.2 Hz), 7.21 (1H, dd, *J* = 2.4 Hz, *J* = 8.0 Hz), 7.14 (1H, dd, *J* = 2.6 Hz, *J* = 9.0 Hz), 6.87 (2H, d, *J* = 8.2 Hz), 6.66 (2H, d, *J* = 8.1 Hz), 5.31-5.26 (1H, m), 4.74-4.68 (1H, m), 2.95-2.75 (2H, m), 2.15-2.05 (2H, m), 1.78 (1H, s), 1.74 (1H, s) 1.64-1.05 (8H, m), 1.02 (9H, s), 0.98 (9H, s), -15.09 (1H, s); ^{13}C NMR (67.8 MHz, C_6D_6) δ 153.24, 149.93, 146.65, 142.90, 142.77, 142.49, 142.13, 141.19, 139.37, 138.91, 131.70, 131.01, 129.87, 128.88, 124.66, 123.58, 122.07, 116.97, 114.94, 80.59, 78.38, 34.14, 31.98, 31.73, 31.11, 28.87, 27.27, 26.69, 26.26.

Bis(4-(*tert*-butyl)-2-(p-tolylsulfinyl)phenyl)amine-*d* (3–*d*): To a well stirred yellow solution of magnesium bis(4-(*tert*-butyl)-2-(*p*-tolylsulfinyl)phenyl)amide **4** (120 mg, 0.106 mmol) in 1 mL of C_6D_6 was added 10 μL (0.246 mmol) of CD_3OD using a gas tight syringe. The resulting yellowish gel was stirred for 12 h and centrifuged (1.5 h, 4000 rpm) to afford a clear supernatant solution, which was decanted and evaporated to dryness (116 mg, off–white solid). The H NMR spectrum corresponds to **3** with the integral of the N–H signal at 8.7 ppm reduced to 19% (81% deuteration).

X-ray crystal structure determinations: CCDC-XXXXXXX (for **3**), CCDC- XXXXXXX (for **5** · $0.5C_5H_{12}$) and CCDC- XXXXXXX (for **6** · $3.5C_6H_6$) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Suitable single crystals for X-ray structure

determination were selected from the mother liquor under an inert gas atmosphere and transferred into protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream of the diffractometer. Intensity data for **3** were collected at 160 K on an Oxford Diffraction SuperNova diffractometer equipped with mirror optics, for **5** · $0.5C_5H_{12}$ at 100 K on a Bruker Nonius KappaCCD diffractometer (graphite monochromator) and for **6** · $3.5C_6H_6$ at 100 K on a Bruker Kappa APEX II Duo diffractometer equipped with an INCOATEC microsource and Quazar mirror optics. Mo*Ka* radiation (λ = 0.71073 Å) was used for all three data collections. Multi-scan absorption corrections for **3** were applied using CrysAlisPro,[23] while SADABS[24] was employed for the other structures. The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 (SHELXS-2014[25] and SHELXL-2014[26] for **3**, SHELXTL NT 6.12 for **5** · $0.5C_5H_{12}$ and **6** · $3.5C_6H_6$).[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All three compounds crystallize with two symmetry-independent molecules in their respective asymmetric units. The asymmetric unit of **6** · $3.5C_6H_6$ contains seven molecules of benzene. The atomic coordinates of the two molecules in **3** and **6** · $3.5C_6H_6$ were tested carefully for a relationship from a higher symmetry space group using the program PLATON.[28] In **6** · $3.5C_6H_6$ a pseudo centre of inversion relationship is found for 88% and 98% of the atoms, respectively, but the space group P-1 would necessitate that the compound is racemic and the model refined in P-1 shows disordered O–atom positions, whereas disorder is not evident in the model in P1 and refinement shows the structure is that of a single enantiomer. In each independent molecule of **3**, one of the *t*Bu groups is disordered over two conformations. Two sets of positions were defined for the atoms of each disordered *t*Bu group and the site occupation factors of the major conformations of these groups refined to 0.558(4) and 0.800(5) for the groups at C20 and C71, respectively. Similarity restraints were applied to the C–C bond lengths and C···C distances involving all disordered C-atoms, while neighbouring atoms within and between each conformation of the disordered *t*Bu groups were restrained to have similar atomic displacement parameters (ADPs). Likewise, disorder is observed for some of the *t*Bu groups in **5** · $0.5C_5H_{12}$. Two alternative orientations each were refined resulting in site occupancies of 0.632(5) and 0.368(5) for the atoms C15–C17 and C15A–C17A, respectively, of 0.541(6) and 0.459(6) for the atoms C57–C59 and C57A–C59A, and of 0.590(6) and 0.410(6) for the atoms C67–C69 and C67A–C69A. The cyclooctene moiety in the second independent molecule is also slightly disordered. Two alternative orientations were refined resulting in site occupancies of 0.652(6) and 0.348(6) for the atoms C81, C82 and C81A, C82A, respectively. Similarity and pseudoisotropic restraints were applied to the ADPs of the disordered atoms and the atoms of the *n*-pentane solvent

molecule. For **6** · $3.5C_6H_6$ similarity and pseudoisotropic restraints were applied to the ADPs of some ligand carbon atoms. The positions of the H atom at nitrogen (N1) in **3** and **6** · $3.5C_6H_6$ were taken from a difference Fourier synthesis and their positional parameters were refined. All other hydrogen atoms were placed in positions of optimized geometry. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 or 1.5 times the equivalent isotropic displacement parameters of their corresponding carrier atoms. Crystal data and refinement details are summarized in Table S1 in the Supporting Information.

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Supporting Information

Chiral (SO)–N–(SO) sulfoxide pincer complexes of Mg, Rh, and Ir: N–H activation and selective sulfoxide reduction upon ligand coordination

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Table S1. Crystal data and refinement parameters of compounds **3**, **5**, and **6**

	3	**5**·0.5 C_5H_{12}	**6**·3.5C_6H_6
formula	$C_{34}H_{39}NO_2S_2$	$C_{44.5}H_{58}NO_2RhS_2$	$C_{55}H_{60}Cl_3NORhS_2$
M (g mol^{-1})	557.81	1611.90	1024.42
crystal system	triclinic	orthorhombic	triclinic
space group	P1	$P2_12_12_1$	P1
a (Å)	9.76176(14)	13.651(2)	12.4011(8)
b (Å)	10.73671(17)	19.562(2)	13.7958(8)
c (Å)	15.8354(2)	30.787(4)	16.2240(9)
α (°)	90.6518(12)	90	73.207(4)
β (°)	107.7749(12)	90	89.745(5)
γ (°)	102.1293(13)	90	72.852(5)
V (Å^3)	1540.10(4)	8221(2)	2529.3(3)
Z	2	8	2
μ (mm^{-1})	0.203	0.553	0.618
D_c (g cm^{-3})	1.203	1.302	1.345
$2\theta_{(max)}$ (deg)	60.8	55.8	57.0
T (K)	160	100	100
reflns collected	61451	124047	151238
indep refln, R_{int}	16643, 0.0235	19603, 0.0588	25616, 0.0408
reflns with $I > 2\sigma(I)$	15464	17689	22502
parameters refined	789	1040	1135
restraints	207	143	201
GOF	1.026	1.052	1.065
$R(F)$ [$I > 2\sigma(I)$ reflns]	0.0340	0.0340	0.0263
$wR(F^2)$ (all data)	0.0910	0.0735	0.0583
$\Delta\rho$ (max; min) [e Å^{-3}]	0.311; –0.249	0.931; –0.458	0.444; –0.439
absolute structure parameter	-0.02(2)	–0.02(2)	0.06(2)